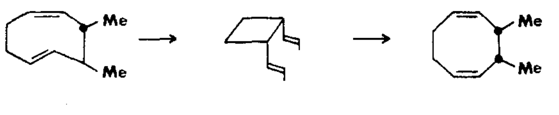
tion about one double bond as well as formal inversion of configuration at one of the asymmetric carbon atoms of **3**.

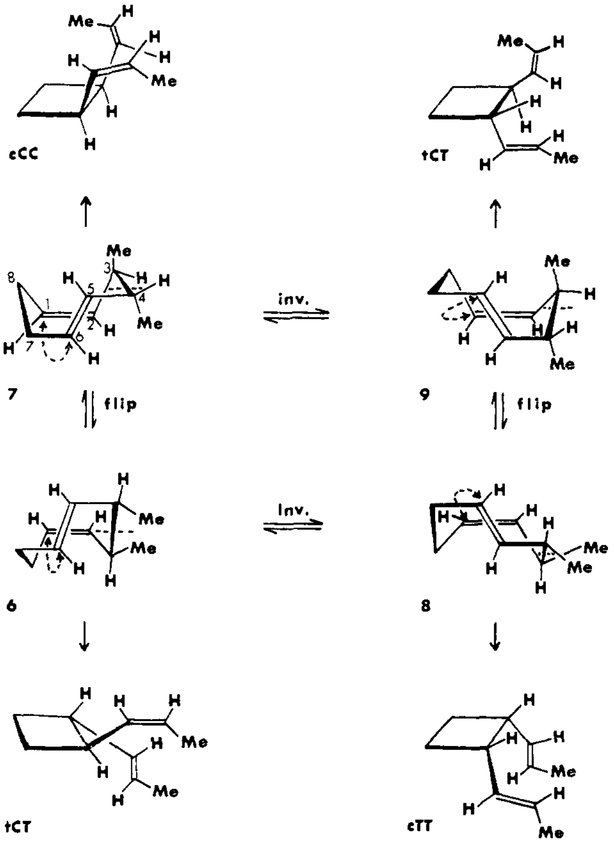
The mechanistic puzzle created by this result is solved by the identification of the minor product as *cis*-1,2-*trans,trans*-dipropenylcyclobutane (cTT), pyrolysis of which is known to give **5** exclusively.[3] In accord with the mechanism **3** → cTT → **5**, we find that shorter pyrolysis of **3** (500 sec) permits the detection of a higher proportion of the intermediate (**5**:cTT = 2.7:1). Again, polymer formation limits the yield of volatiles to 30%, but no other pyrolysis products appear. The overall process thus consists of two successive highly stereospecific Cope rearrangements, the first chair-like and the second boat-like.



3 **cTT** **5**

Two diastereomers of *trans*-3,4-dimethylcycloocta-1,5-diene (**3**) can exist which differ in the axial dissymmetry element associated with the ring. In principle, they should be thermally interconvertible by rotations about the bonds C_6–C_7 and C_4–C_5 (**6** $\rightleftharpoons$ **8** and **7** $\rightleftharpoons$ **9**), by analogy to the racemization of *trans*-cyclooctene.[7] Moreover, just as in the parent *cis,trans*-cycloocta-1,5-diene (**1**)[2], ring flips should rapidly interconvert conformational isomers (**6** $\rightleftharpoons$ **7** and **8** $\rightleftharpoons$ **9**, Scheme I).

Scheme I



It is not known whether **3** prepared by the present method contains one or both of the diastereomers. However, although the inversion barrier is undoubtedly much higher than the conformational one,[2] it might be surmounted at 146.5°. Therefore, even if only one diastereomer results from synthesis, the other might be accessible under the conditions of pyrolysis. In any case, the chair-like Cope rearrangement leading to cTT evidently proceeds from **8**.

It might appear that Scheme I provides a potential mechanism for the frequently observed[3,8,9] thermal racemization and trans $\rightleftharpoons$ cis interconversion of 1,2-dialkenylcyclobutanes. In detail, however, this seems unlikely. Although the racemization [(*RR*)-tCT $\rightleftharpoons$ (*SS*)-tCT)] cannot be formally ruled out, Scheme I requires that a trans → cis transformation of the relationship of the propenyl groups be coupled with a T → C inversion of one of the olefinic geometric configurations. This conflicts with the experimental observations[3] of the reactions tCC $\rightleftharpoons$ cCC and tCT $\rightleftharpoons$ cCT.

In the absence of a stereochemical labeling experiment such as that described here, caution would be advisable in the mechanistic interpretation of the thermal isomerization of the parent compound, *cis,trans*-cycloocta-1,5-diene, to the cis,cis isomer.

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[7] *Cf.* A. C. Cope and B. A. Pawson, *J. Amer. Chem. Soc.*, **87**, 3649 (1965).

[8] G. S. Hammond and C. D. DeBoer, *ibid.*, **86**, 899 (1964).

[9] D. J. Trecker and J. P. Henry, *ibid.*, **86**, 902 (1964).

[10] National Institute of General Medical Sciences Predoctoral Fellow (No. 5-FO1-GM-40662), 1968–1971.

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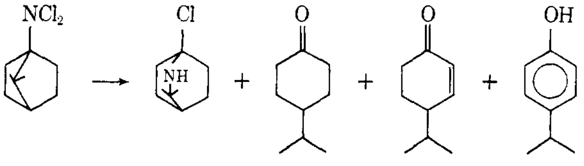
Received August 5, 1972

Rearrangement of 1-*N*,*N*-Dichloroaminoapocamphane with Aluminum Chloride, and Solvolytic Behavior of the 1-Chloro-3,3-dimethyl-2-azabicyclo[2.2.2]octane Product

Sir:

Exposure of *N*,*N*-dihaloamines to aluminum chloride has recently been shown to result in products, after hydrolysis, which derive from alkyl migration to electron-deficient nitrogen.[1] We wish to report that a similar reaction of 1-*N*,*N*-dichloroaminoapocamphane (**1**) with aluminum chloride, in addition to following the expected rearrangement route to **2**, yielded products **3**, **4**, and **5** (*ca.* 40% yield total) arising from *β* scission.



1 2 3 4 5

1, obtained by chlorination of 1-aminoapocamphane[2] with *tert*-butyl hypochlorite in cyclopentane, on treatment with 2 mol of aluminum chloride in methylene chloride at *ca.* −75° provided 1-chloro-3,3-dimethyl-2-

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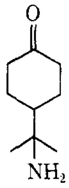
[1] P. Kovacic, J.-H. Liu, E. M. Levi, and P. D. Roskos, *J. Amer. Chem. Soc.*, **93**, 5801 (1971); T. A. Kling, M. B. Nazareno, and P. Kovacic, *ibid.*, **94**, 2157 (1972); P. Kovacic, M. K. Lowery, and P. D. Roskos, *Tetrahedron*, **26**, 529 (1970); S. J. Padegimas and P. Kovacic, *J. Org. Chem.*, **37**, 2672 (1972).

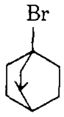
[2] D. N. Kursanov and S. V. Vitt, *J. Gen. Chem. USSR*, **25**, 2401 (1955).

azabicyclo[2.2.2]octane (**2**) in 10% yield. **2**,[3] mp 55–56°, exhibited ir bands at 3280, 2850, 1370, 1350, 1090, 1050, and 775 cm^{-1}, and nmr bands at 1.25 s, (6 H), 1.4 (m, 2 H), 1.7 (s, 1 H), *ca.* 1.7 (m, 1 H), and 2.1 (m, 6 H) ppm. Chemical characterization was accomplished by hydrolysis to the amino ketone (**6**): mp 37–38°; ir bands at 2850, 1700, 1580, 1380, 1360, and 1040 cm^{-1}; nmr bands at 1.12 (s, 6 H), 1.25 (s, 2 H), 1.6 (m, 2 H), and 2.4 (m, 8 H) ppm. Wolff–Kishner reduction of **6** afforded dimethylcyclohexylcarbinamine[4] which was synthesized from α,α-dimethyl-α-cyclohexylacetamide[5] by Hofmann degradation.



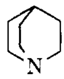
6

Analogous α-chloroamines have been isolated or proposed as intermediates in prior studies entailing *N*-haloamines and either aluminum chloride[1,6] or silver salts.[7] However, **2** appears to be unique in that the chlorine atom is at a bridgehead position of a bicyclic system. Open-chain compounds of the type $[RCH{=}NR_2]^+X^-$ exist as immonium salts.[8] The stability and covalent nature of **2** are most likely associated with the strain involved in introducing a carbon–nitrogen double bond at a bridgehead position.[9] The solvolysis of **2** is of particular interest in regard to bridgehead reactivity. Preliminary data for solvolysis in water or 80% ethanol indicate that **2** reacts appreciably faster than **7**.[10]



7

Another indication of the enhanced reactivity of the bridgehead chloride **2** is the immediate formation of precipitate on contact with aqueous silver nitrate at room temperature. In comparison, 4 hr were employed to effect reaction with **7**.[11] A more detailed kinetic study of the solvolysis of this unusual compound is underway. A related situation was reported[12] by Grob and Sieber in which the positions of the nitrogen and electron-deficient carbon were reversed. On the basis of the observation that the 2-quinuclidinyl cation **8** is somewhat more stable than its carbon counterpart (the bicyclo[2.2.2]-2-octyl cation), they proposed delocalization involving the bridgehead nitrogen.



8

The major nonbasic products, **3**, **4**, and **5**, from rearrangement of **1**, result from β scission of the carbon–carbon bond present in the shortest bridge. These known compounds were identified by comparison of their ir and nmr spectra to those of authentic materials.[13] This type of reaction has been previously encountered[14] with *N*-haloamines. Experiments were carried out to differentiate between polar and radical pathways. Since little or no inhibition was noted in the presence of oxygen, an ionic type fission appears more likely.

Acknowledgment. We are grateful to the National Science Foundation, Eli Lilly and Co., and the Graduate School of the University of Wisconsin—Milwaukee for support of this work.

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[3] Microanalyses were satisfactory.

[4] G. Drefahl, K. Ponsold, and G. Köllner, *J. Prakt. Chem.*, **23**, 136 (1964).

[5] H. Koch and W. Haaf, *Justus Liebigs Ann. Chem.*, **618**, 251 (1958).

[6] T. Sasaki, S. Eguchi, T. Kiriyama, and H. Suzuki, *Syn. Commun.*, **1**, 267 (1971).

[7] P. G. Gassman, *Accounts Chem. Res.*, **3**, 26 (1970).

[8] K. Harada, "The Chemistry of the Carbon–Nitrogen Double Bond," S. Patai, Ed., Interscience, New York, N. Y., 1970, p 259.

[9] For another example, see ref 7.

[10] R. C. Fort, Jr., and P. v. R. Schleyer, *Advan. Alicycl. Chem.*, **1**, 283 (1966).

[11] W. v. E. Doering, M. Levitz, A. Sayigh, M. Sprecher, and W. P. Whelan, Jr., *J. Amer. Chem. Soc.*, **75**, 1008 (1953).

[12] C. A. Grob and A. Sieber, *Helv. Chim. Acta*, **50**, 2531 (1967).

[13] We thank Drs. H. J. Wobben, R. Ter Heide, and R. Timmer for kindly furnishing spectral data on *dl*-cryptone (**4**).

[14] P. Kovacic, M. K. Lowery, and K. W. Field, *Chem. Rev.*, **70**, 639 (1970); D. C. Horwell and C. W. Rees, *Chem. Commun.*, 1428 (1969); J. M. Biehler and J.-P. Fleury, *Tetrahedron*, **27**, 3171 (1971).

[15] Postdoctoral, 1971–1972.

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Received July 31, 1972

Neighboring Group Participation by Bridgehead Nitrogen in Bridged Polycyclic Systems[1]

Sir:

The synthesis of molecules which would appear to extend the limits of Bredt's rule[2] has been the topic of several recent reports.[3] In addition, molecules with double bonds to bridgeheads have been postulated as intermediates in a variety of reactions[4] involving relatively strained bicyclic systems. In view of the experimental results referenced above, we questioned whether the seemingly anomalous stability of the cation **1** might not be due to stabilization of the positive charge by the nonbonding electrons of the bridgehead nitrogen.[5,6]

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[1] Paper XXVI in a series on the Chemistry of Nitrenium Ions. For the previous papers in this series see P. G. Gassman, A. J. Battisti, and K. Shudo, *Tetrahedron Lett.*, in press; P. G. Gassman and G. Hartman, *Chem. Commun.*, 853 (1972).

[2] J. Bredt, H. Thouet, and J. Schmitz, *Ann.*, **437**, 1 (1924); J. Wiseman, *J. Amer. Chem. Soc.*, **89**, 5966 (1967), and references contained therein.

[3] For specific examples see (a) J. A. Marshall and H. Faubl, *ibid.*, **89**, 5965 (1967); (b) N. M. Weinshenker and F. D. Greene, *ibid.*, **90**, 505 (1968); (c) J. R. Wiseman, H.-F. Chan, and C. Ahola, *ibid.*, **91**, 2812 (1969); (d) W. Carruthers and M. I. Qureshi, *Chem. Commun.*, 832 (1969); (e) J. R. Wiseman and J. A. Chong, *J. Amer. Chem. Soc.*, **91**, 7777 (1969); (f) J. R. Wiseman and W. A. Pletcher, *ibid.*, **92**, 956 (1970); and (g) J. A. Marshall and H. Faubl, *ibid.*, **92**, 948 (1970).

[4] For discussions and leading references see ref 3e and 3f. See also R. Keese and E.-P. Krebs, *Angew. Chem., Int. Ed. Engl.*, **10**, 262 (1971).

[5] P. G. Gassman and R. L. Cryberg, *J. Amer. Chem. Soc.*, **91**, 2047 (1969); see also J. O. Reed and W. Lwowski, *J. Org. Chem.*, **36**, 2864 (1971).

[6] When 4,7,7-trimethyl-2-chloro-2-azabicyclo[2.2.1]heptane was solvolyzed in methanol, a significant amount of 2-methoxy-3,3,4-trimethyl-1-azabicyclo[2.2.1]heptane was obtained. It was suggested that the methyl ether was formed from nucleophilic attack of methanol on **1**, which represents the Wagner–Meerwein rearrangement product of the initially formed nitrenium ion. However, a perplexing problem was associated with this hypothesis in that **1** should have been destablized